Intraslab remobilization of nitrogen during early subduction facilitates deep nitrogen recycling: insights from the blueschists in the Heilongjiang Complex in NE China

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Key words: Nitrogen remobilization; subduction zone; blueschist; mélange; Heilongjiang Complex; deep nitrogen recycling

Abstract:

Nitrogen (N) in subducting slab resides in both sediments and altered oceanic crust (AOC). The extent of subduction-zone metamorphic devolatilization of N in these reservoirs determines the amount of remaining N for deep recycling. However, N behavior inside the subduction zone, particularly below the forearc region, remains poorly understood so far. Here, we studied the pillow-shaped epidote-blueschist facies meta-basalts (hereafter refer to as blueschists) in the Heilongjiang Complex in Northeast China, aiming to understand the N behavior during the early subduction stage. Results show that these blueschists contain N (13.9 to 122.6 ppm; average: 51.0 ppm) up to seven times higher than the AOC (including pillow lavas) entering global trenches (N < 19 ppm; average 7 ppm). The N concentrations of the blueschists correlate with the Ba and Th concentrations, indicating that significant N enrichment of the blueschists took place inside the subduction zone in addition to small N enrichment on seafloor. The N concentrations and $\delta^{15}N$ values of the blueschists show two distinct mixing trends, indicating that two types of ammonium (NH_4^+) were added into the blueschists. One is characterized by relatively high abundance and positive $\delta^{15}N$ value ($\sim +3‰$), which can be attributed to the direct assimilation of NH_4^+ in metamorphic fluids derived from the sedimentary components in the mélange. The other is characterized by relatively low abundance and extremely low $\delta^{15}N$ values ($\sim -16‰$). This NH_4^+ is consistent with a product of abiotic reduction of sediment-derived N_2. This study demonstrates that the labile N in sediments released during early subduction can be at least partially (if not all) re-fixed into the more refractory meta-igneous part of the subducting slab, which facilitates the retention of N for deep subduction and recycling.

1. Introduction

Nitrogen (N) recycling across subduction zones is a critical part of geological N cycle on Earth (e.g., Hilton et al., 2002; Johnson and Goldblatt, 2015; Bekaert et al., 2020). Nitrogen in the surface reservoirs (e.g., the atmosphere, hydrosphere and biosphere) can be incorporated into seafloor sediments (by precipitation of organic matter and clay minerals) and altered oceanic crust (AOC; by hydrothermal and/or microbial alteration). The N concentrations of subducting sediments can vary depending on lithology from as low as ~ 10 ppm in sandstones, carbonates and cherts, to as high as ~2400 ppm in the organic-rich top sediments (e.g., Sadofsky and Bebout, 2004; Li and Bebout, 2005). In contrast, AOC commonly show much lower N concentrations in a range of 1.3-18.2 ppm (e.g., Busigny et al., 2005, 2019; Li et al., 2007; Bebout et al., 2018). Even though, AOC may contain a large N inventory at least of the same order of magnitude to the overlying sediments in the subducting slab because of its much larger volume (Li et al., 2007). Inside the subduction zones, part of the slab N may be released back to the surface by metamorphic devolatilization and restored in mantle wedge serpentinites by the infiltration of slab-derived fluids; the remainder will be subducted into the deep mantle (e.g., Hilton et al., 2002, 2010; Bebout et al., 2013; Pagé et al., 2018), which could be subsequently sampled by plume-related magmas (e.g., Dauphas and Marty, 1999; Barry and Hilton, 2016; Halldórsson et al., 2016). Subduction-zone N recycling could thus have potentially impacted the long-term evolution of Earth's surface and interior reservoirs (e.g., Sano et al., 2001; Marty and Dauphas, 2003; Mallik et al., 2018; Bekaert et al., 2020), which however cannot be quantitatively assessed so far because the important knowledge of N retention in the slab inside the subduction zones is not well understood.

Metamorphic rocks from ancient subduction zones provide a window to examine the N behavior in subduction zones (e.g., Haendel et al., 1986; Bebout and Fogel, 1992; Bebout, 1997; Busigny et al., 2003a; Sadofsky and Bebout, 2003; Jia, 2006; Halama et al., 2010; Li et al., 2014; Sievers et al., 2017). Nitrogen isotope ratio can be used as a robust tool to assess N devolatilization because of large magnitudes of isotope fractionations between minerals and the common devolatilized N species (NH_3 or N_2; Li et al., 2021a, 2021b). In general, ^{14}N is preferentially taken by the released NH_3 or N_2, which can result in progressive ^{15}N enrichment in the remaining rocks along prograde metamorphism (e.g., Haendel et al., 1986; Bebout and Fogel, 1992; Mingram and Bräuer, 2001).

68 Nitrogen devolatilization modeling of metasedimentary rocks subducted from the forearc to

69 sub-arc depths in four ancient subduction zones suggested high-degree (~70%) N loss (in form of

70 N_2) in the Catalina Schist (Bebout and Fogel, 1992), medium-degree (~30%) N loss (in form of NH_3)

71 in the European Variscan (Mingram and Bräuer, 2001), and nearly no N loss in the Schistes Lustrés

72 (Busigny et al., 2003a) and Franciscan Complex (Sadofsky and Bebout, 2003). These results imply

73 that the fate of N in the subducted sediments could be strongly variable among different subduction

74 zones, which is speculated to be dependent on the thermal structure of individual subduction zone

75 (e.g., warm for the Catalina Schist vs. cold for the Schistes Lustrés; Busigny et al., 2003b; Bebout,

76 2007a).

77 In contrast, studies on high-pressure (HP) to ultrahigh-pressure (UHP) eclogites observed little

78 loss but retention of N in AOC to the sub-arc depth (Philippot et al., 2007; Halama et al., 2010, 2014;

79 Busigny et al., 2011). This implies that AOC could be more resistant to metamorphic

80 devolatilization than sediments. More interestingly, based on correlation of N and trace element

81 concentrations, Halama et al. (2010) observed potential addition of sediment-derived N to the

82 eclogites in the Raspas Complex (Ecuador) by fluid-rock interactions inside the subduction zone.

83 Similarly, relatively high N concentrations (3-74 ppm) have also been observed in some high-

84 pressure (HP) peridotites from the Central Alps, Raspas Complex (Ecuador) and Almirez Massif

85 (Spain), which are speculated to be a result of admixing of sedimentary N during prograde

86 metamorphism within the subduction zones (e.g., Halama et al., 2010, 2014; Cannaò et al., 2020),

87 although N addition during seafloor alteration is also possible. Nevertheless, these studies imply

88 that part of the sedimentary N could be recaptured by the meta-igneous part of the subducting slab

89 during prograde metamorphism. This process, if widely occurs inside the subduction zone, may play

90 a critical role to promote the deep recycling of slab N. However, it is still unclear how common this

91 process is inside the subduction zone, and in particular, whether it can occur in the forearc region

92 where significant N devolatilization from sediments could be initiated (e.g., Bebout and Fogel,

93 1992).

94 In this study, aiming to understand the N behavior in the early subduction stage in the forearc

95 region, we investigated the N concentrations and isotope compositions, as well as major and trace

96 elements of epidote-blueschist facies meta-basalts (hereafter refer to as blueschists) from the

97 Heilongjiang Complex in Northeast China (NE China). These blueschists still retain pillow shaped,

98 which clearly indicates that their protoliths were from the topmost parts of ancient AOC. The

99 epidote-blueschist facies metamorphism occurred in 198-175 Ma (see Zhou and Li, 2017 and

100 reference therein) with peak metamorphic conditions of 320-450°C and a peak pressure of 0.9-

101 1.1GPa (e.g., Zhou et al., 2009), which is equivalent to a subduction depth of ~40 km.

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103 ## 2. Geological background and samples

104 ### 2.1 Regional geology

105 Northeast China is geologically comprised of several micro-continental blocks (**Fig. 1a**; Sengör

106 et al., 1993; Jahn, 2004; Li, 2006). Its western part consists of the Songliao, Xing'an and Erguna

107 blocks, which all belong to the Central Asian Orogenic Belt. These blocks mark the broad collision

108 zone between the North China Craton in the south and the Siberian Craton in the north following

109 the closure of the Paleo-Asian Ocean (Fig. 1a). Its eastern part consists of the Heilongjiang Complex

110 in the west, the Jiamusi Block in the middle, and the Nadanhada Terrrane in the east (Fig. 1b), which

111 is a late Triassic-Cretaceous accretionary terrane formed by the westward subduction of the Paleo-

112 Pacific Plate (e.g., Zhou et al., 2014).

113 The Heilongjiang Complex is an HP metamorphic belt over-thrusted onto the western margin

114 of the Jiamusi Block along the north-south directed Mudanjiang Fault (F1 in Fig. 1b), which was

115 later truncated by the Yilan-Yitong Fault (F2; Zhou et al., 2009; Zhou and Li, 2017). The HP

116 Heilongjiang Complex is characterized by occurrence of blueschists, together with serpentinites,

117 greenschist-facies marble, two-mica schists, muscovite-albite schists, quartz schists, quartzites and

118 minor amphibolites (e.g., Li et al., 1999; Wu et al., 2007; Zhou and Li, 2017). Previous studies have

119 identified that the Heilongjiang Complex was a tectonically juxtaposed mélange (Wu et al., 2007;

120 Zhou et al., 2009, 2010; Zhu et al., 2015, 2017) as a result of an east-west directed closure of an

121 ancient ocean, which was likely related to the Paleo-Pacific Ocean (Li et al., 2021c).

122 The blueschists in the Heilongjiang Complex are mainly exposed in three areas, i.e., from south

123 to north, Mudanjiang, Yilan, and Luobei (Fig. 1b). Most previous studies on the blueschists in the

124 Heilongjiang Complex have been focused on the Mudanjiang and Yilan areas (e.g., Zhou et al., 2009;

125 Zhu et al., 2015, 2017; Ge et al., 2017). The Luobei blueschist outcrops are relatively difficult to

126 access and have not been well studied yet. The dating of detrital zircons gave the maximum protolith

127 ages of 288-258 Ma for the Yilan blueschists and 224-213 Ma for the Mudanjiang blueschists,

128 respectively (Zhou et al., 2013; Ge et al., 2017). Ar-Ar and Rb-Sr dating of these blueschists gave

129 the ages of the blueschist-facies metamorphism to be 198-175 Ma in these two places (Wu et al.,

130 2007; Zhou et al., 2009, 2010, 2013; Zhou and Li, 2017).

131 **2.2 Sampling**

132 Twenty-seven blueschist samples were collected from the Mudanjiang (n = 13) and Yilan (n =

133 14) areas for this study. The Mudanjiang blueschists commonly preserve pillow structure and occur

134 as tectonic lens dominantly in greenschist-facies mica schist with locally preserved stratigraphic

135 layers supporting a sedimentary origin (see Zhou et al., 2009; Zhu et al., 2015; Ge et al., 2016 for

136 detail). The Yilan blueschists occur as small blocks, boudins or sheets that range from meters to

137 hundreds of meters in length with well-preserved pillow structures, which spread in in greenschist-

138 facies mica-schist (see Zhou et al., 2009; Zhu et al., 2015; Ge et al., 2016 for detail). All the samples

139 for this study were collected from the inner parts of the pillows or lens. The rims of the pillow or

140 lens and veins were carefully excluded to avoid retrograde metamorphic influence.

141 **2.3 Petrographic description**

142 The detailed petrographic descriptions of both the Mudanjiang and Yilan blueschists have been

143 given by several previous studies in detail (Zhou et al., 2009; Zhu et al., 2015; Ge et al., 2016).

144 Some key information is summarized here. Meta-basalts from the Mudanjiang area have the typical

145 mineral assemblage of sodic amphibole (20-25%), albite (45%-50%), epidote (20-25%), phengite

146 (5-10%) and chlorite (10-15%) (Fig. 2b and 2c). The sodic amphibole is small (0.5-1 mm; Fig. 2b)

147 and its composition ranges from glaucophane to magnesio-riebeckite (Zhou et al., 2009). Chlorite

148 occurs either in the matrix or around glaucophane (Fig. 2b). The schistosity is defined by sodic

149 amphibole, epidote and chlorite (Fig. 2b and 2c). Few fluid inclusions (1 um to 5 um) were observed

150 in some of the phengite but their overall abundance is low.

151 Meta-basalts from the Yilan area are dominantly characterized by the mineral assemblages of

152 sodic amphibole (20-25%), albite (35%-40%), epidote (25-35%), phengite (5-10%) and chlorite

153 (<10%). (Fig. 2). The sodic amphibole is small (0.5-1 mm; Fig. 2e and 2f) and its composition is

154 dominated by ferro-glaucophane (Zhou et al., 2009; Ge et al., 2016). Chlorite occurs either in the

155 matrix or around glaucophane and albite (Fig. 2f). The schistosity is defined by sodic amphibole,

epidote and chlorite (Fig. 2e and 2f). Few fluid inclusions (1 um to 5 um) were observed in some of the phengite but their overall abundance is low.

Overall, the presence of glaucophane and ferro-glaucophane, associated with epidote and phengite, indicates epidote-blueschist facies metamorphism in the Yilan and Mudanjiang meta-basalts (Zhou et al., 2009). The presence of chlorite indicates these samples experienced retrograde metamorphism as well. However, the preservation of the high-Si signature (3.38-3.46 per formula unit) of phengite (Zhou et al., 2009) indicates that the retrograde metamorphic effect is relatively small on the meta-basalts.

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3. Analytical methods

3.1 Whole-rock major and trace elements

Blueschist rock samples were cleaned by removing surface material and further crushed and ground into fine powders (< 200 mesh). Major and trace elements of eleven samples (i.e., the 15HLJ series; see Table 1) were analyzed in the Actlabs (Ontario, Canada) by a simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP or a Varian Vista 735 ICP. Calibration was achieved using 12 USGS and CANMET certified reference materials. The analytical errors are 0.5-5% of the absolute concentrations for major elements depending on abundance and 10% of the absolute concentrations for trace elements. Major and trace elements of the other sixteen samples (i.e., the 19HLJ and 20HLJ sample series; see Table 1) were analyzed at the State Key Laboratory of Continental Dynamics in Northwest University, Xi'an, China. Major elements were measured using a Rigaku RIX 2000 X-ray Fluorescence spectrometer (XRF). Repeated analyses of USGS (BCR-2) and Chinese national rock standards (GSR-1and GSR-3) gave an analytical error better than 5% of the absolute concentrations for major elements (Wang and Liu, 2016). Trace elements concentrations were analyzed by an Agilent 7500a inductively coupled plasma mass spectrometry (ICP-MS). The analytical uncertainty is less than 10% of the absolute concentrations (Liu et al., 2007).

3.2 Whole-rock N concentrations and isotope compositions

Nitrogen concentration and isotope composition of blueschists were analyzed by the offline sealed-tube combustion and extraction methods coupled with carrier-gas isotope ratio mass spectrometry. The analytical details have been described by Li et al. (2021d) and are briefly summarized here. Sample powders were loaded into a one-end sealed quartz tube together with

186 quartz wool and Cu_xO_x reagents. The tube was then put on a custom-made metal manifold to pump

187 overnight, sealed under high vacuum, and combusted at 1000°C for 8 hours for a complete N

188 extraction (Li et al., 2021d). The sample tube was then loaded back into the metal manifold and

189 cracked under high vacuum. The released N_2 was cryogenically purified and quantified by a

190 capacitance manometer. After quantification, the N_2 gas was carried by an ultrahigh-purity helium

191 gas flow to a Thermo Finnegan MAT 253 isotope ratio mass spectrometer for N isotope analysis.

192 All N isotope data were reported by the δ notation, i.e., $\delta^{15}N_{sample} = (^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard}$ -

193 1, where the standard is atmospheric N_2. Based on repeated analyses of samples and two certified

194 reference material, i.e., the low-organic content soil standard (reference values: N = 0.133 wt.%;

195 $\delta^{15}N$ = +6.97‰) and high-organic content sediment standard (reference values: N = 0.52 wt.%; $\delta^{15}N$

196 = +4.32‰), the analytical error is better than 6% (2σ) for N concentration and 0.2‰ (2σ) for $\delta^{15}N$.

197

198 **4. Results**

199 **4.1 Major and trace elements**

200   Whole-rock major and trace element compositions of the Mudanjiang and Yilan blueschists are

201 listed in Table 1. Overall, the blueschist samples have SiO_2 concentrations from 39.81% to 52.32%,

202 total FeO concentrations from 9.58% to 15.91%, MgO concentrations from 2.69% to 6.93%, TiO_2

203 concentrations from 1.57% to 4.56%, and Na_2O concentrations from 2.09% to 5.48%. Both the

204 Mudanjiang and Yilan blueschist samples have high concentrations of rare earth elements (REE)

205 with ΣREE varying from 52.2 to 196.6 ppm for the Mudanjiang blueschists and 104.4 to 295.3 ppm

206 for the Yilan blueschists, respectively. On the diagram of chondrite-normalized REE patterns, the

207 Mudanjiang blueschists show slight enrichments in light REE (LREE), with $(La/Yb)_N$ ratios of 2.5

208 to 4.2 and $(La/Sm)_N$ ratios of 1.3 to 1.9, and relatively gentle right-dipping REE patterns similar to

209 those of enriched mid-ocean ridge basalts (E-MORB; Fig. 3a). Most of the Yilan blueschists display

210 strong enrichments in LREE, with $(La/Yb)_N$ ratios of 5.6 to 18.5 and $(La/Sm)_N$ ratios of 1.6 to 5.9,

211 and steep right-dipping patterns similar to those of ocean island basalts (OIB; Fig. 3b). Three Yilan

212 samples (15HLJ-39, 15HLJ-40 and 15HLJ-41) display flat distribution of LREE and strong

213 depletion in heavy REE (HREE), with $(La/Yb)_N$ ratios of 26.4 to 28.5 and $(La/Sm)_N$ ratios of ~1.3

214 (Fig. 3b). The REE patterns of these three samples have been attributed to the low-degree partial

215 melting of garnet-facies peridotites in which HREEs were retained in garnet in the residue (Zhu et

al., 2015). Nevertheless, consistent with previous studies (Zhou et al., 2009; Zhu et al., 2015; Ge et al., 2017), the overall REE patterns of the Yilan blueschists are indicative of an origin similar to OIB.

4.2 N concentrations and isotope compositions

The N concentrations and $\delta^{15}N$ values of the blueschist samples from Mudanjiang and Yilan are listed in Table 1. The Mudanjiang blueschists display a large range in N concentrations from 13.9 ppm to 83.6 ppm, but a relatively small $\delta^{15}N$ range from −0.5‰ to +3.7‰ (Fig. 4). The Yilan blueschists show large variations in both N concentrations and $\delta^{15}N$ values, which can be subdivided into two groups: group A samples are characterized by relatively high N concentrations (21.2 ppm to 122.6 ppm; average: 87.4 ppm) and positive $\delta^{15}N$ values within a small range of +0.9‰ to +3.2‰ (average: +2.5 ± 0.7‰; 1σ; n = 8); whereas group B samples show relatively low N concentrations (17.3 ppm to 46.9 ppm; average: 33.9 ppm) and large $\delta^{15}N$ variations with strikingly negative values (−3.3‰ to −10.9‰; Fig. 4). It should be noted that, the two sets of samples in group B with distinct REE patterns (Fig. 3b) show no difference in N concentrations and $\delta^{15}N$ values: 17.3 to 39.7 ppm and −3.3‰ to −10.1‰ for samples with strong HREE depletion, 24.3 to 46.9 ppm and −3.8‰ to −10.9‰ for the other group B samples, respectively. This indicates that their N signatures more likely reflect a secondary N rather than original magmatic N. Overall, the $\delta^{15}N$ values of the blueschists from the Heilongjiang Complex overlap with those of basaltic portion of AOC from global oceans, but the N concentrations of the blueschists are significantly higher than those of global basaltic AOC (< 19 ppm; Fig. 4).

5. Discussions

5.1 Nitrogen residence in blueschist

Fixed N in minerals is generally accepted to be in form of ammonium (NH_4^+). Because of the similar ionic radius (IR) and charges between K^+ (IR=1.64 Å; Shannon and Prewitt, 1969) and NH_4^+ (IR=1.67 Å; Sidey, 2016), N can be easily enriched into K-bearing minerals (e.g., micas and alkali feldspars; Yamamoto and Nakahira, 1966; Honma and Itihara, 1981; Bos et al., 1988). The substitution of K^+ by NH_4^+ has been well supported by the positive correlations between N and K_2O concentrations observed in several metamorphic suites (e.g., Bebout, 1997; Busigny et al., 2003a; Busigny and Bebout, 2013; Sievers et al., 2017). Surprisingly, such a correlation has not been

observed in AOC (e.g., Li et al., 2007; Busigny et al., 2019). This may be attributed to more complicated incorporation of N in AOC involving multiple secondary minerals (Staudigel, 2014) and organic matter (Ménez et al., 2012) during alteration of oceanic crust. In addition, NH_4^+ can also be assimilated by Na^+- or Ca^{2+}-bearing minerals due to the similar ionic radius between NH_4^+ and Na^+ (IR=1.39 Å; Shannon and Prewitt, 1969) and the replacement of $Ca^{2+}+Mg^{2+}$ by $Al^{3+}+NH_4^+$ (e.g., Honma and Itihara, 1981; Watenphul et al., 2010; Li et al., 2021d).

In the studied blueschists, the N concentrations do not correlate with Na_2O and MgO concentrations, but K_2O concentrations (Fig. 5). This suggests that most of N resides as NH_4^+ in the K-bearing minerals, which are dominated by phengite in the studied samples. Phengite has also been demonstrated to be the major host mineral for N in rocks that have experienced HP and UHP metamorphism (e.g., Li et al., 2014; Halama et al., 2017). In addition, few fluid inclusions observed in the phengite crystals may also contain N but their contribution to the overall N concentrations of blueschists should be small due to their minor abundance. Nevertheless, although some degree of retrograde metamorphism has been observed in the samples (Fig. 2), the majority of N hosted by phengite should not be significantly affected because of the good preservation of phengite (Zhou et al., 2009).

5.2 Effect of metamorphic devolatilization

To assess the metamorphic devolatilization effect on the blueschist samples, we adopted the method of Busigny et al. (2003a) by comparing the variations of multiple fluid-mobile elements (e.g., K, Rb and Cs). This model is based on the different compatibilities among K, Rb and Cs during devolatilization, in which Cs is most strongly fractionated into the fluids, followed by Rb and K (Melzer and Wunder, 2000). The changes of K, Rb and Cs abundances through progressive devolatilization can be described by Equation (1):

$$R_{rock}^f = R_{rock}^0 \times F^{(1/K_D-1)} \tag{1}$$

where R_{rock}^0 and R_{rock}^f represent the initial and final elemental ratios (e.g., Rb/K and Cs/Rb) of rock before and after devolatilization, respectively. F is the fraction of element remaining in the rock after devolatilization. K_D is the ratio of distribution coefficients for the Cs-Rb (K_D^{Cs-Rb}) or Rb-K (K_D^{Rb-K}) system (Busigny et al., 2003a for detail). Considering that K, Rb, Cs and NH_4^+ dominantly reside in K-bearing minerals (i.e., phengite in our case), elemental ratios among K, Rb,

275 Cs and NH$_4^+$ in phengite largely reflect those of whole rock (Zack et al., 2001). Consequently,

276 K_D^{Cs-Rb} and K_D^{Rb-K} values of phengite are employed in the modeling (Table 2). It should be noted

277 that the employed K_D^{Cs-Rb} and K_D^{Rb-K} values of phengite in the modeling are the data from

278 experiments at 600 °C and 2 GPa (Table 2), which are so far the lowest temperature and pressure

279 with available K_D values for phengite (Busigny et al., 2003a). Because the K_D^{Cs-Rb} and K_D^{Rb-K}

280 values of phengite decrease with decrease in temperature and pressure (Busigny et al., 2003a), their

281 values at 320-450°C and 0.9-1.1GPa for the studied blueschist (Zhou et al., 2009) would be smaller.

282 Thus, the employment of data from high temperature and pressure in our modeling may cause some

283 uncertainty, but it should not affect the semi-quantitative constraint on the devolatilization effect.

284 On the diagram of molar abundances of Rb versus Cs (Fig. 6a) and K versus Rb (Fig. 6b), blueschists

285 from Mudanjiang and Yilan are broadly distributed along a linear line instead of following the

286 devolatilization trends illustrated by the dashed curves. This suggests that the effect of metamorphic

287 devolatilization on these fluid-mobile elements is minor. To further examine the effect of

288 metamorphic devolatilization on N, N/K molar ratios are plotted against δ^{15}N values on Fig. 6c.

289 Because ^{15}N is more enriched in minerals than in N$_2$ or NH$_3$ (Li et al., 2021a, 2021b), metamorphic

290 devolatilization would lead to a progressive decrease in the N/K ratio with increase in the δ^{15}N value

291 of the rocks (e.g., Bebout and Fogel, 1992; Mingram and Bräuer, 2001). However, this trend is not

292 observed in the studied blueschists (Fig. 6c), which consistently suggests that the effect of

293 metamorphic devolatilization on N in these blueschists is minor.

294 **5.3 Nitrogen enrichment in protoliths on seafloor**

295   It is noted that the protoliths of the blueschists from Mudanjiang (E-MORB) and Yilan (OIB)

296 are different to normal mid-ocean ridge basalts (N-MORB; Zhou and Li, 2017; Fig. 3). As a result,

297 the initial N inherited from their magmatic sources in these protoliths could be slightly different.

298 Both fresh N-MORB and less contaminated E-MORB have δ^{15}N values of ~ −3‰ to −5‰ (e.g.,

299 Javoy and Pineau, 1991; Marty and Humbert, 1997; Marty and Zimmermann, 1999; Marty and

300 Dauphas, 2003; Li et al., 2007). In contrast, OIB show highly variable δ^{15}N values from −3‰ to

301 +15‰ (e.g., Exley et al., 1987; Marty and Dauphas, 2003; Halldórsson et al., 2016), which could

302 be attributed to recycling of crustal N into their magmatic sources. Nevertheless, the initial N

303 inherited from their magmatic sources should be very low in abundance (< 2 ppm) due to the low

304   solubility of N in mafic magmas (Libourel et al., 2003). Consequently, their original magmatic N

305   signature can be easily overprinted by addition of secondary N during seafloor weathering. Because

306   the protoliths of all the studied blueschist samples were pillow basalts, they should have undergone

307   low-temperature alterations on seafloor similar to those of the topmost part of global oceanic crust.

308   Consequently, we can reasonably assume that the N concentrations and isotope signatures of the

309   protoliths of the Mudanjiang and Yilan blueschists, despite their origin, should be similar to those

310   of the upper section of AOC, which are commonly characterized by sedimentary-like positive $\delta^{15}N$

311   values (Fig. 4; Busigny et al., 2005, 2019; Li et al., 2007; Bebout et al., 2018), although some

312   negative $\delta^{15}N$ values were observed in the basalts of ODP sites 801 and 1149 as the availability of

313   sedimentary N was diminished (Li et al., 2007).

314   **5.4 Element remobilization inside the subduction zone**

315   **5.4.1 Major and trace element evidence**

316   Besides seafloor alteration, fluid-rock interactions inside the subduction zone may also add N

317   into the meta-igneous part of the slab (e.g., Halama et al., 2010, 2017). Some elements, such as Ba,

318   U, Th and K, can be used to distinguish between these two processes (e.g., Bebout, 2007a, 2007b;

319   Halama et al., 2010).

320   Fluid-rock interactions inside the subduction zone can result in greater enrichment of Ba than

321   K in the rock, whereas seafloor alteration does the opposite (Bebout, 2007a, 2007b). Fig. 7a

322   illustrates the comparison between Ba and K concentrations that are normalized to Th

323   concentrations to remove the effect of magmatic fractional crystallization (e.g., Bebout, 2007a;

324   Halama et al., 2010). The blueschist samples from the Heilongjiang Complex show higher Ba/Th

325   ratios that deviate from the seafloor alteration trend defined by modern AOC (e.g., ODP Sites 801,

326   1149 and 504) but are close to the metamorphic enrichment trend defined by high-grade eclogites

327   (e.g., those from the Raspas Complex and Samana Peninsula; Sorensen et al., 1997; John et al., 2004;

328   Halama et al., 2010). In addition, oceanic crust can assimilate significant amounts of U during

329   seafloor alteration (Staudigel et al., 1996; Staudigel, 2014), which produces a steep trend in the

330   Th/U and Th diagram (Fig. 7b). In contrast, the studied blueschists have high Th concentrations and

331   high Th/U ratios, which display a trend opposite to the seafloor alteration trend but again consistent

332   with the metamorphic enrichment trend defined by high-grade eclogites. Therefore, the Th

333   enrichment observed in these blueschists is likely indicative of reaction with HP metamorphic fluids,

334   which has been observed in other HP and UHP metabasite blocks (Fig. 7b; e.g., Sorensen et al.,

335   1997; Saha et al., 2005; also see data compilation in Bebout, 2007a, 2007b, 2013). In summary,

336   major and trace elemental data of the studied blueschists show clear signatures of metasomatic

337   overprint by HP metamorphic fluids inside the subduction zone.

338   **5.4.2 Subduction-zone N enrichment in blueschists**

339   Resolving fluid-rock metasomatism inside the subduction zone from seafloor alteration in

340   above discussions provides a framework to explain the N data. The N concentrations of the

341   Mudanjiang blueschists and the Yilan-group A blueschists positively correlate with Ba (Fig. 8a) and

342   Th concentrations (Fig. 8b). Since these Ba and Th enrichments are attributed to fluid-rock

343   interactions inside the subduction zone (Bebout, 2007a, 2007b, 2013), the majority of N enrichment

344   in these blueschists samples can be consistently considered to take place inside the subduction zone.

345   Compared with the Yilan-group A blueschists, the Yilan-group B blueschists commonly show much

346   lower Ba and Th concentrations, suggesting much less metasomatic effect on the group B

347   blueschists. It should be noted that the group A and B samples occur randomly in the outcrops

348   without specific distribution pattern. This indicates that the fluid-rock interaction inside the

349   subduction zone is highly heterogeneous, consistent with observations from other subduction-zone

350   mélange settings (e.g., Breeding et al., 2004; Spandler et al., 2008). Nevertheless, the Yilan-group

351   B blueschists are much richer in N than global AOC, indicating that these blueschists were able to

352   assimilate significant amounts of N. Overall, the significantly higher N concentrations in blueschists

353   relative to AOC may reflect that low-temperature alteration on seafloor is less efficient to enrich N,

354   whereas the high-temperature and high-pressure conditions inside the subduction zone may promote

355   more efficient N fixation into meta-igneous rocks (Fig. 4).

356   **5.4.3 Source and mechanisms for N enrichment of blueschists**

357   To determine the N source and detailed mechanism for the N enrichment in the blueschists

358   inside the subduction zone, we examined the relationship between the N concentrations and $\delta^{15}N$

359   values of the blueschists (Fig. 4). The Mudanjiang blueschists and the Yilan-group A blueschists

360   show a $\delta^{15}N$ range of $-0.5‰$ to $+3.7‰$, falling into the isotope range ($-0.9‰$ to $+7.3‰$) of the top

361   section of AOC which is considered to assimilate dissolved NH_4^+ in seawater or derived from

362   overlying sediments (Busigny et al., 2005, 2019; Li et al., 2007). The high N concentrations (up to

363   ~123 ppm) of the Mudanjiang blueschists and the Yilan-group A blueschists also require a source

364   containing abundant N, consistent with sediments (e.g., Sadofsky and Bebout, 2004; Li and Bebout,

365   2005). Consequently, N source of the Mudanjiang blueschists and the Yilan-group A blueschists can

366   be attributed to the sedimentary component in the mélange. This is also supported by the elevated

367   Th and Ba concentrations in these blueschists (Figs. 7-8). The Mudanjiang and Yilan-group A

368   blueschists have Ba/Th ratios of 25 to 421, consistent with those of clay-rich sedimentary rocks of

369   21 to 458 but smaller than those of sedimentary carbonate of 700 to 2751 (Plank, 2014). This clearly

370   points to a pelitic sedimentary source in mélange, which is consistent with the field observation that

371   blueschists of Heilongjiang Complex are closely associated pelitic mica schist (Zhou et al., 2009).

372   Employing a two-endmember mixing model (Li et al., 2007), the N concentrations and isotope

373   compositions of the Mudanjiang blueschists and the Yilan-group A blueschists can be fitted by the

374   addition of ^{15}N-enriched NH_4^+ with a $\delta^{15}N$ value of +3‰ into rocks with an initial N concentration

375   of about 14 ppm and a $\delta^{15}N$ value of ~ +1‰ (Fig. 4). This mixing trend could be interpreted by

376   heterogeneous addition of sedimentary N into the protoliths of the blueschists with N of ~14 ppm

377   and $\delta^{15}N$ of ~ +1‰. The mixing trend is still valid if consider that the protoliths of blueschists had

378   heterogeneous N concentrations and isotope compositions similar to the upper branch of data of

379   ODP Sites 801 and 1149 samples (Li et al., 2007; **Fig. 4**). In a simplified scenario of heterogeneous

380   addition of sedimentary NH_4^+ with $\delta^{15}N$ value of +3‰ into the protoliths of the blueschists with

381   relatively homogenous N (~14 ppm and ~ +1‰), this gives $\delta^{15}N$ value of +2.0‰ to +2.2‰ for

382   sediment-derived dissolved NH_4^+ in fluids employing the isotope fractionation of +1.0‰ to +0.8‰

383   (Li et al., 2021b) between phengite and dissolved NH_4^+ in fluids at temperature condition (320-450

384   ºC; Zhou et al., 2009) of epidote-blueschist facies metamorphism. Furthermore, a mass-balance

385   calculation suggests that 36-89% of N (corresponding to 7.9-109.1 ppm N) in the Mudanjiang and

386   Yilan-group A blueschists could come from sedimentary NH_4^+ (Fig. 4).

387   The Yilan-group B blueschists all have negative $\delta^{15}N$ values as low as ~ −11‰, apparently

388   different from those of subducting sediments (+5.2 ±1.6‰; see data complication in Li et al., 2014).

389   Instead, the Yilan-group B data can be fitted by addition of ^{15}N-depleted NH_4^+ with a $\delta^{15}N$ value of

390   ~ −16‰ (Fig. 4). Notably, a similar ^{15}N-depleted NH_4^+ source has been observed in the ODP sites

801 and 1149 basalts (Li et al., 2007) and the UHP rocks with hydrothermally altered protoliths from the Sulu belt in eastern China (Li et al., 2014). An abiotic reduction of N_2 to NH_4^+ by Fe^{2+}-bearing minerals associated with kinetic isotope fractionation has been proposed to account for the formation of this extremely ^{15}N-depleted NH_4^+ (Li et al., 2007, 2014). Although abiotic N_2 reduction in these cases occur before subduction, it does not preclude the occurrence of abiotic N_2 reduction inside the subduction zone if favorable conditions to the reaction are met. In mafic rocks such as the studied blueschists, Fe(II) is abundant and can act as an efficient reductant to abiotically reduce N_2 at 300-500 ºC and high-pressure conditions (Brandes et al., 1998; Li et al., 2014). Therefore, we consistently employ this mechanism to account for the ^{15}N-depleted NH_4^+ endmember (−16‰) in the Yilan-group B blueschists, which is equivalent to a $\delta^{15}N$ value of −15.0‰ to −15.2‰ for dissolved NH_4^+ in fluids considering the isotope fractionation of +1.0‰ to +0.8‰ between phengite and dissolved NH_4^+ in fluids at 320-450 ºC (Li et al., 2021b). Although N_2 inside the subduction zone could come from both metamorphic devolatilization of sediments (e.g., Bebout and Fogel, 1992) and partial melting of the mantle wedge, the latter is unlike to occur given the low-temperature conditions (320-450 ºC) for the formation of the blueschists in the Heilongjiang Complex. Therefore, the enriched N in the Yilan-group B blueschists should be still sourced from the ambient sediment components in the mélange. At 320-450 ºC, the $\delta^{15}N$ difference between dissolved NH_4^+ and N_2 in fluids released from the sedimentary source with same N isotope composition is +5.6‰ to +4.2‰ (Li et al., 2021a), which implies that the $\delta^{15}N$ value of dissolved N_2 in fluids is −3.6‰ to −2.0‰. This requires a kinetic isotope fractionation of −11.4‰ to −13.2‰ between the product NH_4^+ and N_2 in fluids, which is consistent with the kinetic isotope fractionation of −11‰ to −16‰ for abiotic N_2 reduction observed in previous studies (Li et al., 2007, 2014). Accordingly, a mass-balance calculation suggests that a minimum of 19-72% of N (corresponding to 3.3-36.0 ppm N) in the Yilan-group B blueschists could come from abiotic N_2 reduction (Fig. 4).

The local oxygen fugacity may vary strongly at a small scale in the mélange zone (Tumiati et al., 2015), which could result in coexistence of N_2 and NH_4^+ in subduction-zone fluids (e.g., Jackson et al., 2021) although the relative abundances of N_2 and NH_4^+ in fluids could be highly variable. This could induce different N-fixation mechanisms between the Mudanjiang and Yilan-group A blueschists (i.e., direct NH_4^+ assimilation) and the Yilan-group B blueschists (abiotic N_2 reduction

to NH_4^+). The Mudanjiang and Yilan-group A blueschists were likely able to access abundant fluids that have been interacted with sediments (Fig. 9), as revealed by their significantly elevated Ba, Th and N concentrations (Fig. 8), which favors direct NH_4^+ assimilation. In contrast, the relatively low Ba, Th and N concentrations of the Yilan-group B blueschists indicate that the fluids reacted with these blueschists contained much less Ba, Th and NH_4^+, likely due to interactions with other blueschists along their flow path. The lack of NH_4^+ in fluids made N_2 contribute dominantly to blueschists through abiotic N_2 reduction (Fig. 9), although this reaction is less efficient in supplying NH_4^+. Consequently, the Yilan-group B blueschists gained relatively less amounts of NH_4^+ with strong ^{15}N depletion.

5.4.4 Implications to N recycling in subduction zones

The discussion above demonstrates that the devolatilized sedimentary N (either in form of NH_4^+ or N_2) can be at least partially re-fixed by the meta-igneous components of subducting slab inside the subduction zone. This process can transfer N from susceptible sediments to more refractory meta-igneous components in the mélange at the early stage of subduction.

Mélange is a common feature of modern-style subduction zones (Nielsen and Marschall, 2017). Field studies on the exhumed HP mélange zones have suggested that the thickness of mélange zones could vary from hundreds of meters to several kilometers (Bebout, 1991; Marschall et al., 2006). The low-seismic-velocity materials on the upper part of several modern subduction zones (Abers, 2005), which possibly represent the mélange material, vary from 1 to 10 km in thickness (Marschall and Schumacher, 2012). If we assume that the mélange is composed of subducting sediments with an initial weighted average N concentration of 299 ppm (Sadofsky and Bebout, 2004; Li and Bebout, 2005) and AOC with an initial weighted average N concentration of 7 ppm (Li et al., 2007; Bebout et al., 2018; Busigny et al., 2019), a ballpark estimate on the N re-fixation efficiency (i.e., the fraction of the devolatilized sedimentary N that can be re-fixed by the igneous components in the mélange) is illustrated in Fig. 10. The modeling results show that the re-fixation efficiency is strongly controlled by the relative thickness between sediments and AOC that are incorporated into the mélange zone (Fig. 10). Taking the modern Circum-Pacific subduction zones (representing ~70% of global subduction zones in length) as an example, even applying the maximum degree of sedimentary N loss (~40%; Bebout and Fogel, 1992; Bebout et al., 1999) during the epidote-

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blueschist metamorphism in the Catalina Schist (an exceptionally hot subduction zone), the released N from the sediments (average thickness: 794 m) can be efficiently re-fixed if the mélange contains >850-meter AOC (Fig. 10). The required thickness of AOC for efficient re-fixation of devolatilized sedimentary N is even smaller to account for the diminished N devolatilization in cold subduction zones with geotherm of 8°C/km (Busigny et al., 2003a), which may be the case for most of modern subduction zones (Penniston-Dorland et al., 2015). It should be noted here that our modeling of the AOC thickness is conservative because (i) samples in this study were from inner parts of pillow basalts, which likely have experienced less degree of metasomatism than the rims of the pillows, and thus less degree of N enrichment; (ii) the devolatilized sedimentary N could also be re-fixed by the meta-peridotites of subducting slab or serpentinites in the mantle wedge (Halama et al., 2014; Pagé et al., 2018; Cannaò et al., 2020), which are also common components of mélange in subduction zones (e.g., Spandler et al., 2008) but not considered in our modeling due to the loose constraints of N characteristics on these components. Incorporating these parameters can further reduce the thickness of AOC required to re-fix the devolatilized sedimentary N. In turn, the meta-igneous components in the mélange in most of subduction zones can efficiently re-fix the devolatilized sedimentary N.

The K-bearing phases, such as phengite, are the major host of N in metamorphosed AOC (e.g., blueschists, eclogites). Attributed to the stability of phengite over large temperature and pressure ranges (up to ~300 km) in subduction zones (Poli and Schmidt, 1995; Schmidt, 1996; Watenphul et al., 2010), N can be well retained beyond the sub-arc depth. Although some degrees of N loss from phengite may occur during further prograde metamorphism (Halama et al., 2017), significant amounts of N have been observed in the phengite in the UHP eclogites from the Sulu belt (eastern China), which has been subducted to >120 km or even > 200 km (Xu et al., 1992; Ye et al., 2000). This suggests that N can be well retained and recycled into the deep mantle.

6. Conclusions

The pillow-shaped blueschists in Northeast China provide a good opportunity to examine the N behavior at the early stage of subduction. These blueschists contain N concentrations seven times in average higher than AOC. The concentration correlations between N and other elements, such as

478   Ba, Th, indicate that most of the N in the blueschists was added inside the subduction zone. The

479   relationship between the N concentrations and $\delta^{15}N$ values of these blueschist indicates that two

480   types of NH_4^+ was added to the studied blueschists. The first type of NH_4^+ is characterized by a

481   positive $\delta^{15}N$ value, likely directly derived from devolatilization of sediments. This type of N is

482   significantly enriched in the blueschists that have undergone intensive interaction with metamorphic

483   fluid. The other type of NH_4^+ is characterized by strong ^{15}N depletion, likely generated by abiotic

484   reduction of sediment-derived N_2. This type of N is enriched in the blueschists that have undergone

485   limited interaction with metamorphic fluid. These results show that the meta-igneous components

486   of the slab can efficiently re-fix the devolatilized N from the sedimentary portion of the slab, which

487   facilitates the retention of slab N for deep subduction and recycling.

488

489 **Declaration of Competing Interest**

490   The authors declare that they have no known competing financial interests or personal

491 relationships that could have appeared to influence the work reported in this paper.

492

493 **Acknowledgements**

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Figures captions

Fig. 1. Geological sketch map of Northeast China (modified after Han et al., 2020). (a) Tectonic subdivisions of Northeast China showing multiple micro-continental blocks. (b) Map of the Jiamusi Block and adjacent areas showing the spatial distribution of the Heilongjiang Complex from the Mudanjiang area in the south, the Yilan area in the center, to the Luobei area in the north. The sample locations for this study are marked by stars. Abbreviations: F1 = the Mudanjiang Fault; F2 = the Yilan-Yitong Fault; F3 = the Dunhua-Mishan Fault; F4 = the Yuejinshan Fault; F5 = the Tanyuan-Xiguitu Fault; F6 = the Hegenshan-Heihe Fault; F7 = the Xar Moron-Changchun Fault.

Fig. 2. Photographs of field outcrops and thin sections of blueschists from the Heilongjiang Complex. (a) outcrop of the Mudanjiang blueschist showing well-preserved pillow structure; (b) thin section of blueschist sample 15HLJ-05B from Mudanjiang (plane polarized light); (c) thin section of blueschist sample 15HLJ-01 from Mudanjiang (plane polarized light); (d) outcrop of the Yilan blueschist showing well-preserved pillow structure; (e) thin section of blueschist 15HLJ-39 from Yilan (plane polarized light); (f) thin section of blueschist 15HLJ-41 from Yilan (plane polarized light). Abbreviations: Gl: glaucophane; Ab: albite; Ph: phengite; Ep: epidote; Ch: chlorite; Qtz: quartz.

Fig. 3. Chondrite-normalized REE patterns for blueschists showing an affinity of enriched mid-ocean ridge basalts (E-MORB) for the Mudanjiang blueschists (a) and an affinity of ocean-island basalts (OIB) for the Yilan blueschists (b). The compositions of E-MORB and N-MORB are from Gale et al. (2013); and OIB from Sun and McDonough (1989).

Fig. 4 Diagram showing the nitrogen concentrations and $\delta^{15}N$ values of the blueschists from the Heilongjiang Complex in Northeast China. For comparison, the data of global altered oceanic crust (AOC), including Site 801 and 1149 (Li et al., 2007), Site 1256 (Bebout et al., 2018) and Site 504 (Busigny et al., 2019), are also shown. Compared with AOC (N < 19 ppm), the blueschist samples are significantly more enriched in N, but show similar $\delta^{15}N$ distribution patterns. The blueschist data can be interpreted by mixing of two types of ammonium: one with $\delta^{15}N$ value of +3‰, and the other with $\delta^{15}N$ value of ~ -16‰. Numbers along the curves mark the fractions of added ammonium by increment of 10%. See text for detailed discussion. Note that, on x-axis, N concentration is plotted in logarithmic scale from 1 ppm to 19 ppm and non-logarithmic scale from 19 ppm to 150 ppm. The vertical grey dashed line marks the N concentration of 19 ppm. The error bars of N concentrations and $\delta^{15}N$ values are smaller than the symbols and not shown in the diagram.

Fig. 5. Comparison of N concentrations with the concentrations of K_2O (a), Na_2O (b) and MgO (c). Positive correlation is only observed between N and K_2O concentrations. This suggests that nitrogen (in form of NH_4^+) is primarily resided in K-bearing minerals (i.e., phengite in blueschists), rather than Na- or Ca-bearing minerals.

43   Fig. 6. Diagrams comparing the molar abundances of Rb, Cs, K, N and δ^{15}N values of the
44   blueschists to infer the devolatilization effect. In panels a and b, the solid blue and black lines
45   are linear fittings of the Mudanjiang and Yilan blueschist data (note that one outlier from Yilan
46   group A blueschists obviously falling outside the other datasets in Fig. 6a was excluded for liner
47   fitting); grey dashed curves represent the devolatilization trends modeled by Equation (1) for
48   Mudanjiang and Yilan blueschist data. Numbers along the curves are the fractions of elemental
49   loss after devolatilization. In panel c, the lack of negative correlations between the N/K molar
50   ratios and δ^{15}N values suggests that the effect of metamorphic devolatilization on N is minor.
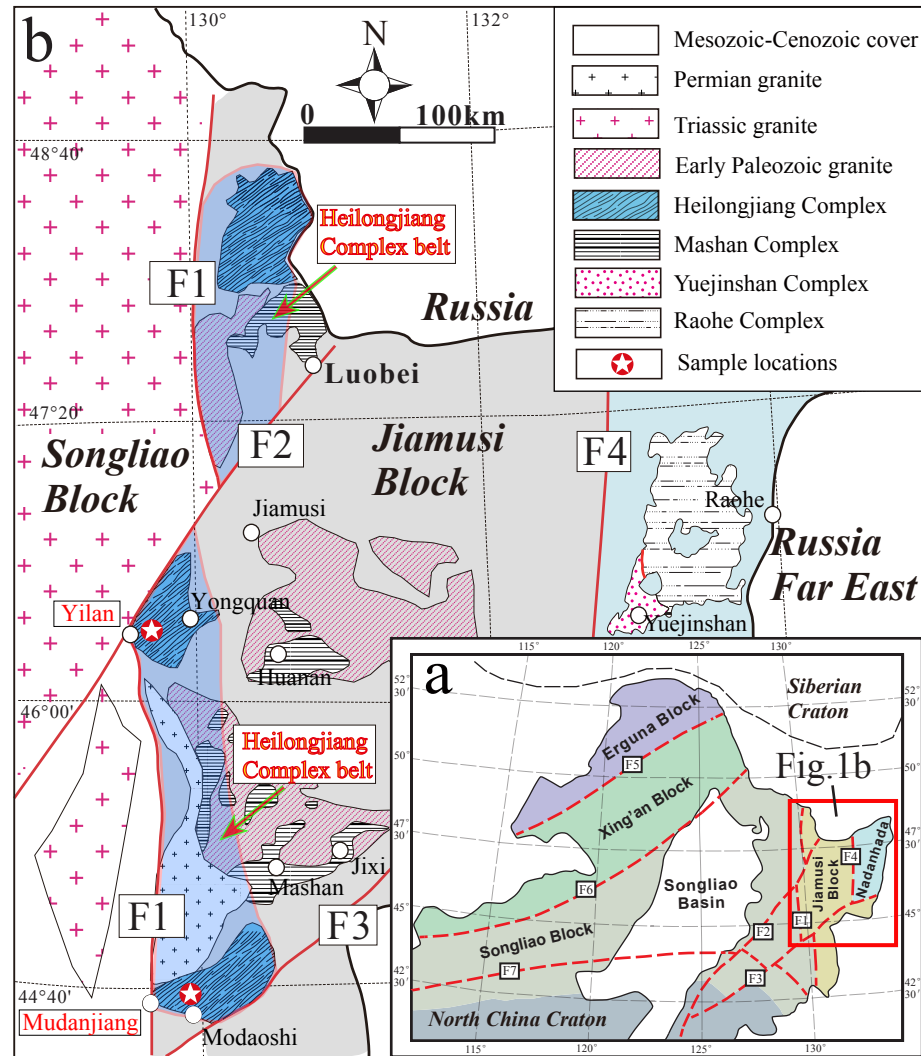51
52   Fig. 7 Diagrams showing the different effects of low-temperature seafloor alteration and
53   subduction-zone metamorphism on (a) K and Ba concentrations (both normalized to Th
54   concentration) and (b) Th/U ratios and Th concentrations. The seafloor alteration effect trends
55   (grey arrows) are defined by the data of modern altered oceanic crust (AOC), including ODP
56   sites 801 and1149 (Kelley et al., 2003), Site 801 (Kelley et al., 2003) and Site 504 (Bach et al.,
57   2003). The subduction-zone metamorphic effects (pink arrows) are defined by high-grade
58   eclogites from the Raspas Complex (Eclogites-1) (John et al., 2004; Halama et al., 2010) and
59   Samana Peninsula (Eclogites-2) (Sorensen et al., 1997). The compositions of E-MORB and N-
60   MORB (Gale et al., 2013) and OIB (Sun and McDonough, 1989) are also plotted for reference.
61   The blueschists from the Heilongjiang Complex show trends distinct to the seafloor alteration
62   effect but consistent with the subduction-zone metamorphic effect.
63
64   Fig. 8. Correlations of N concentrations with Ba concentrations (a) and Th concentrations (b)
65   of the blueschists from the Heilongjiang Complex. The solid lines are linear regressions for the
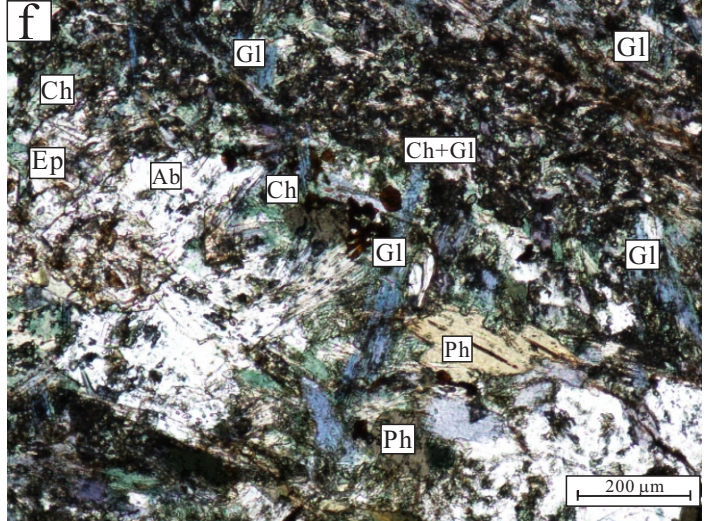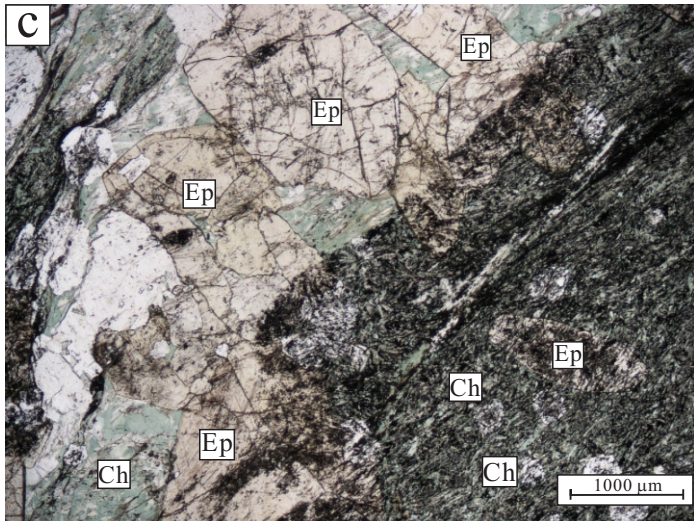66   Mudanjiang blueschists and the Yilan-group A blueschists (see text for discussion).
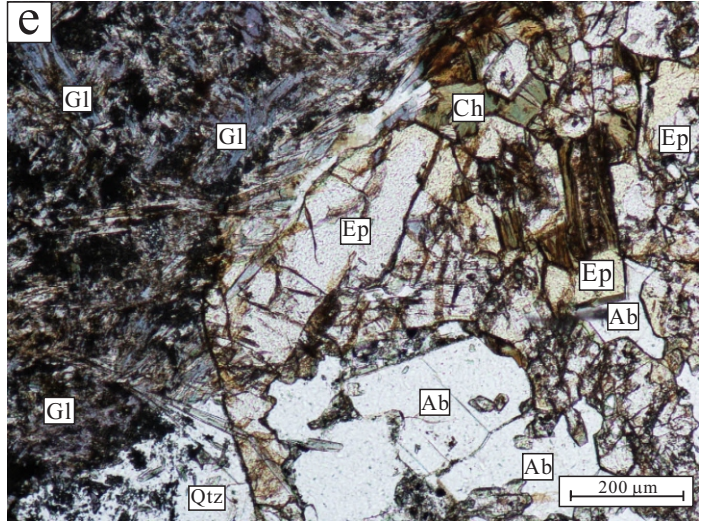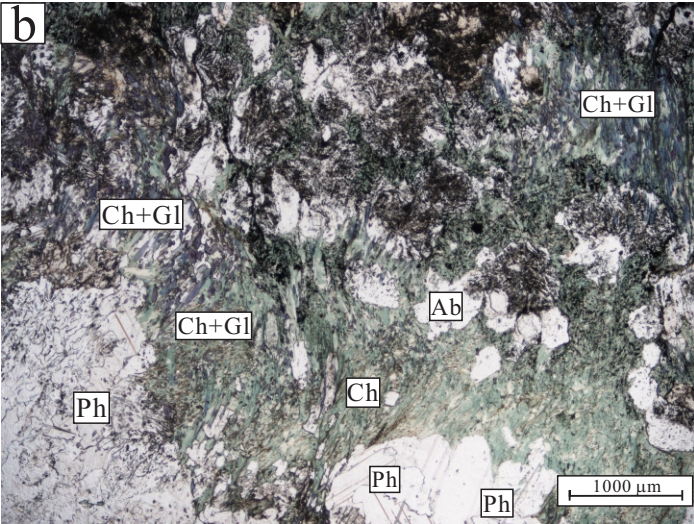67
68   Fig. 9. Schematic diagram (not to scale) showing the N transfer from the sedimentary
69   components to the meta-igneous components in the mélange of a subduction zone (modified
70   from Bebout and Penniston-Dorland, 2016). Two N transfer pathways are illustrated in the
71   diagram. One is that N is released from sediments as NH_4^+, which is subsequently re-fixed by
72   the meta-igneous components through fluid-rock interaction. The other is that N is released
73   from sediments as N_2, which is reduced into NH_4^+ and subsequently re-fixed by the meta-
74   igneous components.
75
76   Fig. 10. Diagram showing the relationship between the N re-fixation efficiency and the
77   thickness of sediments and altered oceanic crust (AOC) that are incorporated into the mélange.
78   The numbers on the curves represent the thickness of AOC. The parameters used in the
79   modeling include average density (1.64 g/cm^3) and porosity (38.5%) of subducting sediments
80   from Plank and Langmuir. (1998), average density (2.93 g/cm^3) and porosity (12%) of
81   subducting AOC from Johnson and Pruis (2003), the initial weighted average N concentrations
82   of 299 ppm for sediments (Sadofsky and Bebout, 2004; Li and Bebout, 2005) and 7 ppm for
83   AOC (Busigny et al., 2005, 2019; Li et al., 2007; Bebout et al., 2018), and the final average N
84   concentration of 51 ppm (this study) for the blueschist-facies igneous rocks. The horizontal
85   grey bar represents the maximum fraction of N loss of sediments during the early-stage
86   subduction. The vertical grey bar represents the average thickness of the subducting sediments

2

87   along the Circum-Pacific subduction zones (Plank and Langmuir, 1998; Clift, 2017). The
88   python code for modeling is available at https://github.com/GeoCan22/N-Re-fixation-
89   Efficiency-Modeling

a

Mudanjiang

E-MORB
N-MORB
OIB

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Smaples/Chondrite

b

Yilan

group A
group B

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Smaples/Chondrite

sediments

AOC

oceanic lithosphere

crust

forearc mantle wedge

mélange zone

fluid flow

NH_4^+: N is released from sediments in form of NH_4^+, which is assimilated by the meta-igneous components

N_2 : N is released from sediments in form of N_2

NH_4^+: product of abiotic N_2 reduction is assimilated by the meta-igenous components

Table1. N concentrations, $\delta^{15}N$ values, major and trace element compositions of blueschists from Heilongjiang Complex, Northeast China.

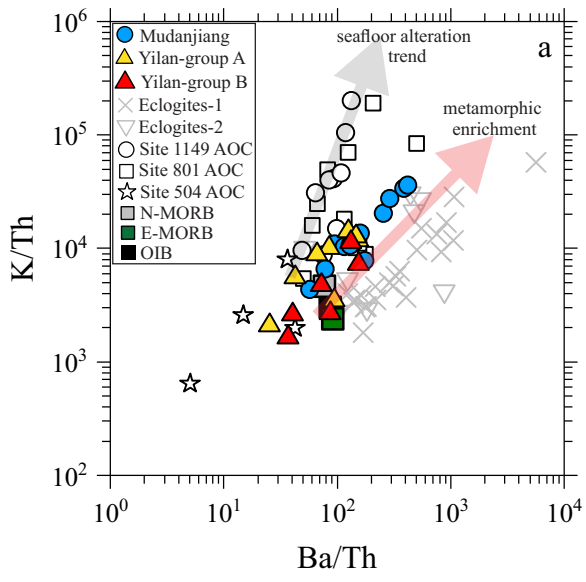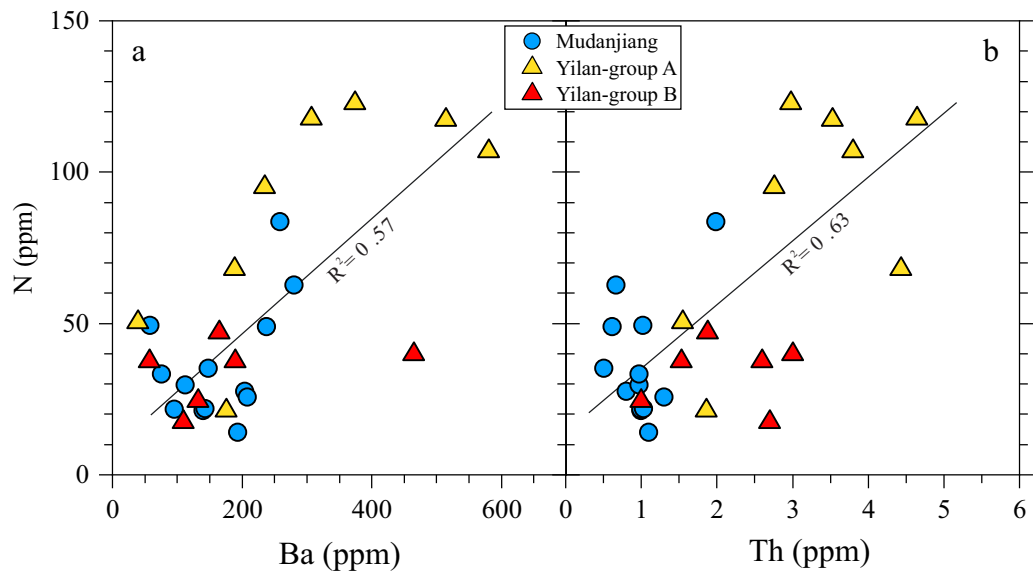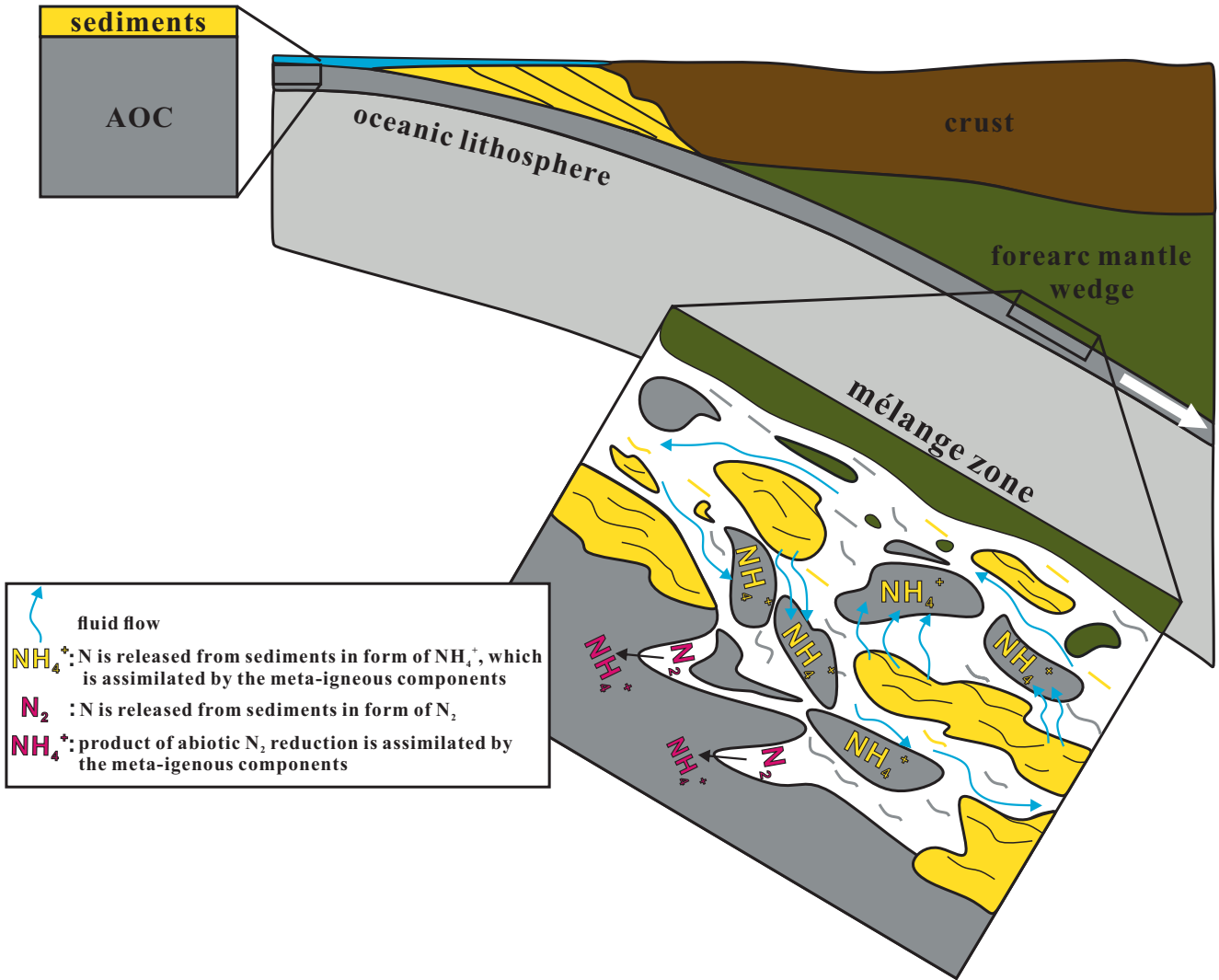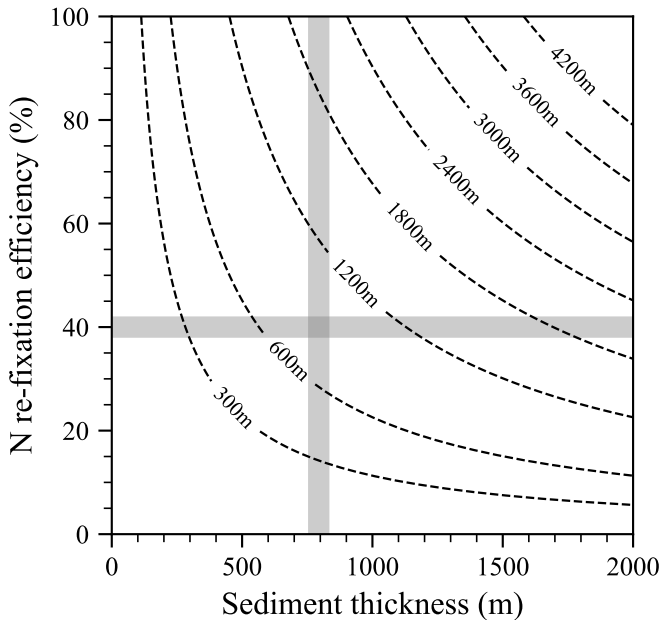|	Mudanjiang blueschists												
	20HLJ-14	20HLJ-14-1	20HLJ-14-2	20HLJ-14-3	20HLJ-15	20HLJ-15-1	20HLJ-15-2	20HLJ-15-3	15HLJ-06	15HLJ-02	15HLJ-05B	15HLJ-01	15HLJ-04
SiO_2	45.22	44.21	44.37	42.78	43.65	44.73	46.65	43.15	44.75	45.1	42.87	45.29	40.01
TiO_2	2.48	2.33	2.47	2.24	1.98	1.57	2.06	3.20	1.971	2.105	2.715	2.15	2.368
Al_2O_3	16.36	15.98	15.85	15.61	17.20	13.96	18.43	15.79	14.21	16.27	17.24	16.77	15.51
TFe_2O_3	12.46	12.91	11.76	11.91	12.90	11.41	12.98	14.95	11.3	13.23	15.37	12.36	12.21
MnO	0.12	0.17	0.12	0.23	0.10	0.11	0.08	0.11	0.128	0.144	0.144	0.159	0.178
MgO	3.78	6.93	4.74	5.00	2.99	2.97	3.27	3.02	2.69	3.94	3.83	3.55	4.01
CaO	8.92	7.01	9.38	11.63	9.10	11.05	5.48	8.26	12.6	9.24	9.64	10.49	14.47
Na_2O	3.85	3.98	3.62	2.94	3.21	3.51	3.81	3.09	3.86	3.66	2.29	3.6	3.08
K_2O	1.38	0.53	1.22	0.77	2.51	1.67	2.89	2.53	1.95	1.43	2.12	1.31	1.03
P_2O_5	0.39	0.37	0.36	0.35	0.27	0.29	0.31	0.62	0.31	0.38	0.36	0.52	0.37
LOI	4.61	5.19	5.75	6.51	5.75	8.30	3.73	5.07	5	2.9	3.37	4.09	7.12
Total	99.57	99.61	99.64	99.97	99.66	99.57	99.69	99.79	98.77	98.4	99.94	100.3	100.3
Li (ppm)	23.0	37.1	24.5	28.4	33.4	29.1	34.9	32.0	n.a	n.a	n.a	n.a	n.a
Be	1.28	1.07	1.46	1.02	1.20	0.81	1.35	1.94	2	1	1	1	< 1
Sc	31.6	29.7	27.0	26.3	33.7	25.9	32.9	31.9	24	28	31	27	27
V	214	197	207	220	247	199	259	300	204	203	277	231	214
Cr	224	226	219	224	111	98.4	105	164	190	210	270	220	230
Co	41.7	90.6	67.2	75.1	43.0	70.6	60.4	50.6	25	46	42	40	52
Ni	147	212	180	213	122	119	118	123	100	150	140	160	170
Cu	49.4	58.9	71.2	65.6	50.3	51.0	42.9	50.7	40	40	50	50	40
Zn	98.7	135	110	105	89.2	90.5	97.2	112	70	110	120	90	120
Ga	15.4	18.1	15.7	20.2	16.8	13.3	17.4	24.6	12	16	20	18	17
Ge	1.33	1.36	1.33	1.74	1.28	0.97	1.20	2.43	< 1	1	2	2	1
Rb	37.1	15.1	33.5	21.7	54.7	37.2	65.0	64.9	50	36	54	34	24
Sr	235	212	248	412	234	185	164	314	204	212	281	281	371
Y	33.2	29.7	29.4	32.3	26.1	19.1	28.4	58.3	25	30	36	30	29
Zr	184	182	182	168	123	95.3	131	320	153	161	214	165	183
Nb	18.6	19.2	19.0	17.7	10.4	7.98	11.2	30.9	14	15	20	17	17
Cs	1.74	0.65	1.56	1.02	2.94	2.10	3.33	4.25	2.1	1.5	2.4	1.5	1.1
Ba	143	58.6	113	76.1	238	148	280	259	204	140	208	132	96
La	16.0	13.8	12.3	15.5	8.75	6.20	10.1	27.5	13.5	16.4	19.9	15	13.8
Ce	36.1	33.0	29.1	34.7	21.7	16.2	24.0	62.1	29.6	35	44.3	34.7	32.4
Pr	4.56	4.19	3.82	4.43	2.80	2.16	3.16	9.12	4.04	4.77	5.87	4.64	4.38
Nd	22.1	19.9	18.7	21.4	14.3	11.1	16.2	44.8	19	22.7	27.6	21.8	20.3
Sm	5.51	5.22	4.89	5.38	4.03	3.09	4.45	10.9	4.9	5.8	6.9	5.5	5.3
Eu	1.80	1.76	1.60	1.82	1.40	1.07	1.57	3.34	1.71	1.95	2.44	2.01	1.84
Gd	5.73	5.48	5.03	5.47	4.27	3.29	4.80	11.0	5.3	6.4	7.8	6.1	5.8
Tb	0.94	0.89	0.84	0.90	0.74	0.56	0.83	1.81	0.8	1	1.2	1	0.9
Dy	5.77	5.45	5.20	5.60	4.61	3.50	5.15	11.1	5	5.8	7.2	5.7	5.4
Ho	1.19	1.09	1.06	1.14	0.94	0.71	1.06	2.16	1	1.2	1.4	1.1	1.1
Er	3.31	2.98	2.98	3.20	2.63	1.95	2.90	5.87	2.8	3.3	4	3.2	3
Tm	0.49	0.43	0.44	0.48	0.39	0.29	0.42	0.86	0.38	0.44	0.57	0.44	0.44
Yb	3.10	2.71	2.72	2.96	2.38	1.79	2.61	5.27	2.5	2.8	3.6	2.8	2.9
Lu	0.48	0.40	0.42	0.46	0.36	0.27	0.39	0.78	0.36	0.44	0.55	0.41	0.42
Hf	4.10	3.93	4.05	3.73	2.98	2.32	3.21	7.36	3.4	3.9	4.9	3.8	4.1
Ta	1.20	1.20	1.22	1.15	0.67	0.56	0.73	1.97	0.9	1	1.4	1.1	1.1
Pb	0.77	0.80	0.84	1.56	0.59	0.43	0.82	1.78	< 5	< 5	< 5	< 5	< 5
Th	1.03	1.02	0.98	0.97	0.62	0.51	0.67	1.99	0.8	1	1.3	1	1
U	0.49	0.38	0.42	0.52	0.39	0.25	0.39	0.76	0.4	0.5	0.6	0.5	0.5
N (ppm)	21.9	49.2	29.7	33.3	48.9	35.0	62.6	83.6	27.5	21.1	25.6	21.6	13.9
$\delta^{15}N$ (‰)	0.5	2.1	3.6	1.6	0.5	1.2	1.0	2.2	3.7	1.4	-0.5	1.7	1.1

							Yilan blueschists							
	19HLJ-04	19HLJ-07	19HLJ-08	19HLJ-09	19HLJ-10	19HLJ-11	19HLJ-12	20HLJ-31-1	20HLJ-31-2	20HLJ-31-3	15HLJ-38	15HLJ-39	15HLJ-40	15HLJ-41
SiO_2 (wt.%)	47.34	39.86	52.32	51.08	51.10	50.64	50.32	47.31	45.84	45.67	46.04	47.24	45.49	45.63
TiO_2	2.64	2.50	3.26	2.69	2.93	2.97	2.86	2.89	1.96	2.92	4.556	3.465	3.303	3.126
Al_2O_3	14.91	11.28	13.79	14.58	14.86	13.46	13.14	14.63	13.30	18.51	12.59	12.35	12.21	13.16
TFe_2O_3	12.66	10.82	12.55	11.30	11.51	12.01	13.93	13.12	9.58	10.85	15.91	15.31	13.02	13.43
MnO	0.19	0.22	0.07	0.11	0.08	0.10	0.07	0.16	0.14	0.13	0.132	0.109	0.125	0.125
MgO	6.15	6.32	5.04	5.46	5.32	5.90	3.66	6.23	4.92	5.30	4.94	4.88	4.28	4.28
CaO	9.00	11.92	1.89	3.06	2.30	2.25	3.44	8.41	10.10	8.00	7.62	5.26	10.31	9.63
Na_2O	2.85	2.09	3.00	2.79	2.77	3.23	5.48	3.21	5.16	3.26	3.83	3.78	4.48	4.08
K_2O	0.61	3.35	5.09	5.37	5.37	4.96	2.95	0.30	0.39	0.78	1.37	2.64	0.85	1.49
P_2O_5	0.47	0.72	0.22	0.25	0.32	0.82	1.90	0.35	0.34	0.36	0.85	1.25	1.25	1.22
LOI	2.89	11.15	2.77	3.50	3.49	3.62	2.15	3.12	7.96	3.94	2.7	2.77	3.49	4.4
Total	99.71	100.23	100.00	100.19	100.05	99.96	99.90	99.73	99.69	99.72	100.5	99.06	98.81	100.6
Li (ppm)	19.9	30.3	34.3	31.8	36.6	36.8	21.4	8.84	35.7	11.6	n.a	n.a	n.a	n.a
Be	1.47	1.46	1.67	2.11	2.06	1.99	1.53	1.60	1.31	0.88	3	4	3	3
Sc	29.5	19.1	20.3	18.6	19.2	15.1	15.1	35.7	14.6	35.7	9	6	6	6
V	245	122	92.1	78.4	109	92.4	90.9	306	131	256	232	176	164	157
Cr	148	19.5	40.4	28.3	34.3	12.5	9.43	155	138	44.3	30	50	50	50
Co	42.5	27.2	31.6	27.9	28.3	17.7	11.6	51.3	51.6	45.4	46	34	44	35
Ni	94.4	24.6	44.3	38.2	43.4	11.6	9.12	64.7	133	32.6	90	70	90	60
Cu	58.3	12.4	13.6	11.7	12.4	12.6	11.8	85.5	104	72.1	10	< 10	10	20
Zn	108	125	128	116	105	137	95.3	111	79.3	88.3	240	240	230	210
Ga	21.6	16.5	19.3	20.9	21.5	20.4	14.4	20.8	11.2	22.0	39	41	40	36
Ge	1.52	1.44	1.70	1.64	1.74	1.58	1.37	1.46	1.37	1.33	1	1	1	1
Rb	9.86	71.1	105	104	106	89.9	52.2	3.95	11.5	10.9	16	35	12	16
Sr	219	592	15.9	61.7	45.8	58.6	111	371	186	494	691	368	970	1024
Y	40.5	32.6	17.6	17.4	22.2	32.2	29.1	33.8	20.9	34.5	39	38	35	33
Zr	218	149	190	219	225	265	253	192	103	200	428	515	500	475
Nb	24.4	38.4	39.4	43.1	45.4	68.6	68.0	22.0	32.4	28.0	26	33	30	29
Cs	0.19	2.02	2.33	2.48	2.86	2.70	1.42	0.025	3.51	0.049	< 0.5	0.8	0.7	1.4
Ba	164	235	374	581	514	308	188	56.8	39.1	175	227	465	110	190
La	21.8	23.2	21.0	51.8	27.4	50.2	29.2	18.8	22.3	22.6	39.8	40.5	37.7	35.7
Ce	47.0	51.8	47.4	100	54.7	105	67.5	42.3	44.8	47.9	101	101	95.8	90.9
Pr	6.55	7.38	4.74	10.5	5.62	11.4	9.27	5.35	5.14	5.78	14.7	15	13.8	12.9
Nd	29.7	34.0	18.5	36.4	22.7	45.5	46.8	26.1	22.7	27.1	75.8	70.8	68.6	65.8
Sm	7.59	8.33	3.77	5.65	4.92	8.96	11.5	6.63	4.86	6.76	21.7	20.7	19.3	18.5
Eu	2.36	2.64	1.23	1.47	1.51	2.94	3.28	2.09	1.60	2.23	8.13	7.16	6.77	6.49
Gd	7.87	7.91	3.93	5.05	5.11	8.90	10.4	6.68	4.62	6.68	23.9	20	19.6	18.4
Tb	1.28	1.16	0.63	0.68	0.82	1.30	1.46	1.08	0.70	1.09	2.8	2.8	2.5	2.2
Dy	7.62	6.41	3.87	3.90	4.84	7.04	7.26	6.40	3.98	6.45	12.1	11.6	10.8	9.9
Ho	1.49	1.17	0.77	0.77	0.93	1.26	1.21	1.26	0.76	1.27	1.6	1.5	1.4	1.3
Er	4.08	2.99	2.15	2.27	2.51	3.35	3.02	3.39	2.01	3.42	2.9	2.8	2.5	2.4
Tm	0.56	0.39	0.31	0.32	0.35	0.45	0.39	0.49	0.29	0.49	0.26	0.24	0.22	0.19
Yb	3.49	2.23	1.88	2.01	2.09	2.65	2.32	2.92	1.69	2.90	1.2	1.1	1	0.9
Lu	0.50	0.30	0.27	0.30	0.30	0.39	0.35	0.43	0.25	0.42	0.14	0.13	0.13	0.1
Hf	5.13	3.71	4.58	5.20	5.42	6.17	5.94	4.68	2.49	4.71	11.4	12.4	11.2	10.8
Ta	1.50	1.95	2.53	2.70	2.86	3.69	3.24	1.35	1.83	1.66	1.7	2.1	2	1.9
Pb	1.78	5.83	1.12	1.18	1.19	1.22	1.32	2.17	4.14	2.53	< 5	< 5	< 5	< 5
Th	1.88	2.76	2.98	3.80	3.53	4.64	4.44	1.53	1.55	1.87	2.1	3	2.7	2.6
U	0.56	0.57	0.41	0.53	0.62	1.18	1.11	0.47	0.38	0.77	0.8	0.8	1.4	0.8
N (ppm)	46.9	95.0	122.6	106.9	117.2	117.7	67.9	37.4	50.29	21.20	24.3	39.7	17.3	37.5
$\delta^{15}N$ (‰)	-10.9	2.7	3.1	2.9	2.6	2.1	2.5	-7.8	3.2	0.9	-3.8	-10.1	-3.3	-3.3

n.a. data not analyzed.

Table 2. Exchange coefficients and initial elemental ratios employed in the progressive devolatilization modeling.

	K_D	R_{rock}^0
Rb-K	1.62 [a]	0.11[b]
Cs-Rb	0.14 [a]	1.80 [b]

a. The K_D values of Rb-K and Cs-Rb between phengite and fluid at 600 °C, 2GPa were used.

b. The highest molar abundances of K ($\times 10^2$), Rb ($\times 10^4$) and Cs ($\times 10^6$) in each location were employed as their initial molar abundances to derive the initial elemental ratios.